NEW METHOD FOR THE FIXATION OF ATMOSPHERIC NITROGEN

BY

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A THESIS

PRESENTED BY

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AND

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Test of a new method for the fixation of atmospheric nitrogen.

Of all the chemical elements which occur in large quantities on our planet, the element nitrogen is characterized by its almost perfect indifference to chemical attack. We are quite accustomed to this indifference of nitrogen in that practically the only use that we make of it, is as an innert atmosphere to protect other things from oxidation and chemical attack. This however is not the only form in which nitrogen exists. When in combination, nitrogen is characterized by its extreme activity as its use as nitric acid, explosives and other nitro-compounds will testify. When in combination nitrogen plays its most important part in our lives and in all of our industries. Upon it together with phosphates and potash our lives depend. Nitrogen compounds are continually being removed from the soil by plants and they must be replaced again, for plant growth is dependant upon them. This is a problem of the greatest importance, for the replacement must be made either with some nitrogen compound or by the slow method of raising such crops as clover and alfalfa, which dissimilate the nitrogen of the air by means of a bacteria, which exists on their roots. Such plants on dying return to the soil the nitrogen that they have taken out of the atmosphere. Up to the last few years, our needs in the form of nitrogen compounds was

entirely supplied and is still largely supplied by already formed nitrogen compounds. We were dependant on compounds, which were the remains of early plant life,such as Chile saltpeter and the ammonia liquor obtained in the manufacture of gas from coal. In the last decade the demand for such nitrogenous material both for agricultural and industrial purposes has tremendously increased, while on the other hand the supply of Chile saltpeter has been decreasing rapidly. The supply of nitrogen compounds from the manufacture of gas and coke has increased but slowly: and we cannot expect this to maintain the balance, offset by our decreasing saltpeter deposits. It has been estimated that the nitrate fields of Chile contain about 340,000,000 tons of saltpeter, and this with an annual exportation of 2,000,000 tons would only supply the world for the next 120 years. Ekstrom in his estimate of the fields does not expect the supply to last later than 1940. Although experts differ in their estimates, it is quite evident that the day is not far off when the Chile saltpeter deposits will give out. Thus it was highly important that some methods of transferring our superabundant innert nitrogen to the combined state were devised.

There have been three general methods employed in the fixation of atmospheric nitrogen. The first is by the direct oxidation of the nitrogen of the air to nitric acid and nitrates by means of the electric arc. The second general method is the synthesis of ammonia from its elements and the third is by the fixation of nitrogen *with* a metal or metalloid and the subsequent decomposition of the resulting product, producing ammonia. The last process is a true fixation process. A short review of these general processes is as follows.

The first process, that of direct oxidation of the nitrogen of the air to oxides of nitrogen by means of an electric spark, has been known for a long time; but its commercial application after a series of failures is only recent. The first attempt to carry out the oxidation of nitrogen on a commercial scale was made by the Atmospheric Products Co. of Niagra Falls, using the patents of Bradley and Lovejoy. Their first apparatus consisted of a series of small compartments, in each of which an arc was formed between horn shaped electrodes. This was supplanted by a single piece of apparatus in which 6000 arcs were formed per second. This was an iron cylinder, four feet in diameter and five feet long. In the center of this rotated a shaft carrying a series of radial arms, the ends of which were platinum tipped. Six rows of 28 inlet wires each, projected thru the cylinder and ended

in a platinum hook. As the radial arms rotated, the platinum tips passed the platinum hooks and the arcs that were formed were drawn out by the revolutions of the shaft. The arcs were drawn out from four to six inches before going out. The current was supplied by a direct current generator. which gave 8000 volts at .75 ampere. Air was passed into the cylinder at the rate of 11.3 cubic meters per second: and it contained 2.5 percent of nitric oxide when it came out of the cylinder. The nitrogen of the air in contact with the arcs had become oxidized to nitric oxide. The yield is said to have been 87 grams of nitric acid per kilowatt hour of current used. The process although feasible was not commercially successful and the work was discontinued. There are three commercial processes for the oxidation of nitrogen by means of the electric arc. These are the Birkeland-Eyde, the Schonherr and the Pauling processes. They differ principally only in type and design of furnace employed. Practically all of the processes have been in operation since 1905, and the only progress made during that time was in raising the concentration of the oxides of nitrogen in the gaseous mixture as it leaves the furnace. Some progress was also made in simplifying the design of the furnaces employed. The first successful process for the oxidation of nitrogen was that of Birkeland and Eyde.

In the process of Birkeland and Eyde a high voltage flame is formed between two electrodes, consisting of water cooled copper tubes. Flichter in 1861 had demonstrated that when an electric arc was placed in the field of an electromagnet it was drawn out into a thin sheet of flame. Use is made of this in that the electrodes are placed in the field of an enormous horse-shoe magnet. The arc forms itself between the nearest points of the electrodes and is caused by the magnetic field to travel outward, and it travels along the electrodes until the current is reversed. A new flame then starts from the opposit side of the electodes. The current used is a 5000 volt alternating current, at 50 cycles per second. Each reversal of the current forms a new flame. The electrodes are enclosed in a narrow iron furnace, which is lined with refractory brick. In the center of the furnace is the flame chamber, which is from 10 to 15 centimeters wide and two meters high. Air is forced thru the furnace at the base and leaves it at a temperature of 800 to 1000°C, containing about one percent of nitric oxide. The temperature of the flame proper exceeds 3000°C. The gases from the furnaces are first conducted under steam boilers, where they are cooled to 200°C. This excess heat is utalized for power. The gases are next led to the cooling house where they are further cooled to 50°C, in aluminum pipes immersed in running water. The gases then pass

to the oxidation chambers. These are vertical iron cylinders lined with acid proof stone. Here the reaction $2NO$ plus O_2 equals $2NO_2$ is completed. The gas is next led to the absorption towers, which are filled with broken quartz. The gas enters at the base of the towers and passes upward, while water trickling downward thru the tower packing is converted to a solution of nitric acid. The towers are placed in series, and the nitric acid solution becomes more concentrated as it passes from tower to tower: the gas becoming more depleted of its oxides of nitrogen as it travels on. The last traces of NO_2 are removed in the last tower by a sodium carbonate solution, producing nitrite and nitrate of soda. The principal factories using the Birkeland and Eyde process, are at Notodden in Norway where 200,000 horse power obtained from the falls nearby is utilized. The products of these factories are placed on the market as nitrites and nitrates of sodium, calcium and ammonium, and as chemically pure nitric acid.

The process of the Badishe Anilin and Soda-fabrik was invented by Schonherr and Hessberger. The principal underlying the special type of furnace employed, is that when an air current is passed around an alternating current arc in a helical path, the arc is more stable and is in less danger of being blown out. In this furnace the arc is contained in an iron tube 4 inches in diameter and 25 feet in length. The electrodes are at opposit ends of the tube, which

is held vertical. The upper electrode is water cooled. Air is forced thru small openings in the base of the tube and circulates spirally around the arc..The reaction products are drawn off at the top of the furnace and are conducted to absorption towers. The lower electrode is an iron rod, adjustable within a water cooled copper cylinder. The iron is slowly eaten away and it is fed in at the rate of one electrode every three months. These furnaces are used in a plant at Kristianssand in Norway.

The third process was invented by H. and O. Pauling, and it is carried out at Innsbruck in Tirol and in several places in the southern part of France. The arcs are produced between curved electrodes, which are in close proximity at their lower portions and are inclined about 45° from the vertical. The arc starts at the place where the electrodes are the closest together and it is blown upward by the air blast from below. The electrodes are water cooled iron pipes. The arc reaches a length of about one meter. The two unique things in the process are the shape of the electrodes and the use of copper kindling blades, which renew the arc in case it is blown out. The outcoming gases contain about 1.5 percent of nitric oxide. The rest of the process is the same as the preceeding ones.

There are several modifications of the standard processes of nitrogen oxidation, among which are the Thorcsen and the Ellis processes. The Ellis process makes use

of rotating arcs made by a rotating magnetic field.

A process for the fixation of nitrogen,as described in the Zentralblatt fur de Kunstdungen-Industrie, makes use of the fact that oxides of nitrogen result when mixtures of air and a combustable gas are detonated. The inventors claim that the conditions necessary to secure a high yield of oxides of nitrogen have been determined,and that the process is a commercial possibility. The conditions necessary are high temperature and pressure; and the proportion of oxygen present must be greater than that in air. This means that oxygen must be added to the mixture of gases before detonating. Under these conditions a yield of as much as 12 pounds of nitric acid had been obtained from 1000 cubic feet of gas.

The second method for the fixation of nitrogen is thru the synthesis of ammonia. The synthetic production of ammonia from its elements became a commercial possibility only about a year ago; and the first factory for the production of synthetic ammonia is now in the course of construction at Oppau in Germany by the Badische Anilin und Soda-Fabrik. Research work on the synthesis of ammonia had been in progress for many years , but it was principally the work of Haber that brought success to the undertaking. The process is essentially as follows:- The gases nitrogen and hydrogen, mixed in correct proportions, are heated under pressure in the presence of a catalytic agent. Under these conditions a small amount of ammonia is formed. The product is removed by either drawing it directly from the apparatus in liquid

form, or by withdrawing it in the apparatus by means of a suitable absorption agent. Water is the best absorption agent, producing a concentrated solution of ammonia under pressure. The gases not acted upon continue to circulate in the system until acted upon; fresh gases being added to take the place of those removed as ammonia. The amount of ammonia formed depends upon the temperature, the pressure and the nature of the catalyst used. The investigations of Haber have shown that at a temperature of 1000°C, the decomposition of ammonia into its elements is almost quantitative. He found that at 700°C and atmospheric pressure, only .02% of ammonia was obtainable. Thus at these high temperatures the ammonia equilibrium is unfavorable, while at lower temperatures the catalytic action of metals is too slow, so higher pressures had to be used. It was found that under a pressure of 200 atmospheres and a temperature of 650 to 700°C, using as a catalyst pure iron oxide, the catalyst occupying a space of 20 cubic centimeters; and with a gas speed of 250 liters per hour it was easy to obtain 250 grams of ammonia per liter of contact space in an hour. The following is a description of the apparatus used by Haber. The catalytic agent is enclosed in a metal tube. The gas mixture passes into this tube, thru the catalyst, then thru a heat regenerator and into a circulating pump. Leaving this it passes in a countercurrent around the outside of the regenerator tubes and the tube containing the

catalyst, and then it enters this in front and repeats the journney as described. The apparatus is protected against loss of heat by packing it in an insulating material; and then enclosing it in an outer shell, which can withstand the high pressure. The catalyst is kept at a suitable temperature by electrically heating it from within. The whole circulation of gases takes place at a high pressure. Between the heat generator and the circulating pump the gases pass either an absorber or a condenser, depending on which form of product is desired. Considerable difficulty was found in constructing the apparatus, which had to be large enough and at the same time strong enough to withstand the high pressure and temperature. These difficulties however were overcome by suitable construction. The whole apparatus was placed in a bomb-proof chamber to guard against any danger of explosion or of any sudden flames of hydrogen, should the apparatus become defective. Care was taken to keep oxygen out of the apparatus, for at that high pressure an explosion would result. Special devices were placed on the apparatus to watch over the oxygen content; and when a definite percentage of that gas was reached, an alarm was automatically raised. The final and great step i the process was the finding of such catalysers. *AS* ould rapidly combine the nitrogen and hydrogen in sufficient quantities and at lower temperatures than those that had been previously used. Haber tried Osmium and found that its

action was favorable even at 550°C: and when at a pressure of 175 atmospheres, a gas concentration of 8 volumes percent of ammonia was obtained, Osmium could not be used on a commercial scale however, because of its rarity, high price and unpleasant properties. Uranium was also found by Haber to be a very good catalyst, as used in the form of the metal, or as an alloy, or as the nitride, or carbide as produced in the electric furnace. When as the nitride or carbide, it crumbles to a fine powder under pressure and its action even under 500°C is excellent. No water or impurities can be present in the gases when Uranium is used in this way. The following table shows the equilibria obtainable at different temperatures and pressures, when Uranium is used as a catalyst.

Temperatures in degrees Centigrade.	Pressures. 1 atmosphere. Vol. percent NH_3.	100 atmospheres. Vol. percent NH_3.
800	0.011	1.1
700	0.021	2.1
600	0.048	4.5
500	0.13	10.8
400	0.48	...

Good results were achieved with iron and iron oxide as catalysts, when the temperatures were not much above 600°C. Manganese also gives good results under certain conditions: that is when the gases are free from oxygen either free or combined. Molybdenum is an excellent catalyst and it can be

used in the form of molybdic acid or ammonium molybdate. Tungsten will also give good results under suitable conditions. In the course of the investigations it was found that catalysts were made more active by the presence of certain foreign bodies. These have been called promoters; and they are the oxides, hydroxides and salts of the alkalies and alkaline earths. The presence of even a minute quantity of these in many cases will raise the catalytic activity. The promoter can be added either to the already prepared catalyst or to the substances used in its preparation. There were also special poisons found which would hinder or prevent the reaction entirely, although the contact mass did not suffer any noticable chemical change. Oxygen and sulphur are the most violent of these poisons,for their presence even in almost minute quantities in the gases would render the catalyst almost inactive. Thus the contact mass had to be carefully prepared so as to be free from these poisons, and the gases also had to be pure. In the case of the gases the removal of impurities was effected by filtration, washing, conducting over solid absorbants and the like. In a recent German patent it was claimed that by the use of ruthenium as a catalyst, a gas mixture containing 11 to 12 percent NH_3 had been obtained at 450°C and 80 atmospheres pressure. At 175 atmospheres pressure a 20% volume yield was obtained. The catalyst was in the form of a salt of its higher oxide. This yield is the highest of any recorded, but

the use of ruthenium on a commercial scale has not been tried. On the costs and yields of the synthetic process little or no data is available. The fact that German capital has been withdrawing from the other processes of nitrogen fixation and is now backing the synthetic ammonia process, shows that the new process will be able to compete favorably with the others.

The third general method for nitrogen fixation is to combine nitrogen with metals or metalloids and to produce nitrides. cyanides, cyanamides etc. Of these the calcium cyanamidesprocess seems to be the one best known.

Cyanamide, like many other things was the result of the discovery of the electric furnace, for it was the electric furnace that induced continued research along the line of nitrogen fixation. Siemens and Halske were the first to undertake the problem with the use of the electric furnace. This was in 1895. They worked on the process of Prof. H. Mehner, which consisted in conducting nitrogen thru a fused mixture of sodium carbonate and carbon. In the same year they made experiments with the process of Prof. Adolph Frank and Dr. Nicodem Caro. Their process consisted of subjecting a mixture of barium carbide. sodium hydroxide, potassium hydroxide and carbon at a high temperature to the action of steam and nitrogen. The inventors however soon learned that dry nitrogen was essential to the sucess of the process. In 1898 it was found that barium carbide alone

heated to a temperature of 700 to 800°C readily absorbed nitrogen and formed a product, in which about 30 percent of the nitrogen present was in the form of barium cyanide and the remaining 70 percent was in the form of barium cyanamide. The reactions are as follows:

$$BaC_2 + N_2 = Ba(CN)_2$$

$$BaC_2 + N_2 = BaCN_2 + C$$

Calcium carbide reacts in somewhat the same manner, except that the temperature required is from 1100° to 1200°C. The resulting product is also somewhat different, being exclusively in the form of cyanamide. Calcium carbide can be manufactured at a lower cost and it has the further advantage of having a lower molecular weight. A fusion of cyanamide with alkaline salts readily converts it into the cyanide. The process for the manufacture of calcium cyanamide is in brief as follows: For the production of calcium carbide, lime and coke are mixed in the proper proportions to produce an 80 percent pure carbide. The mixture is placed in a three phase electric furnace and the temperature is raised to the formation temperature of the carbide. The product is tapped off from the side of the furnace into iron cars. After cooling the calcium carbide is crushed and powdered and is packed into cylindrical cans. In the axis of each can is a cylindrical paper core. The can with the carbide is set in a brick walled oven, slightly larger than the can, and is covered with an iron lid. A carbon

pencil is run thru the paper core in the axis of the can. Upon the passage of the electric current the carbide is heated, nitrogen is admitted to the can and absorption takes place very readily at between 1100 to 1200°C. The reaction is as follows:

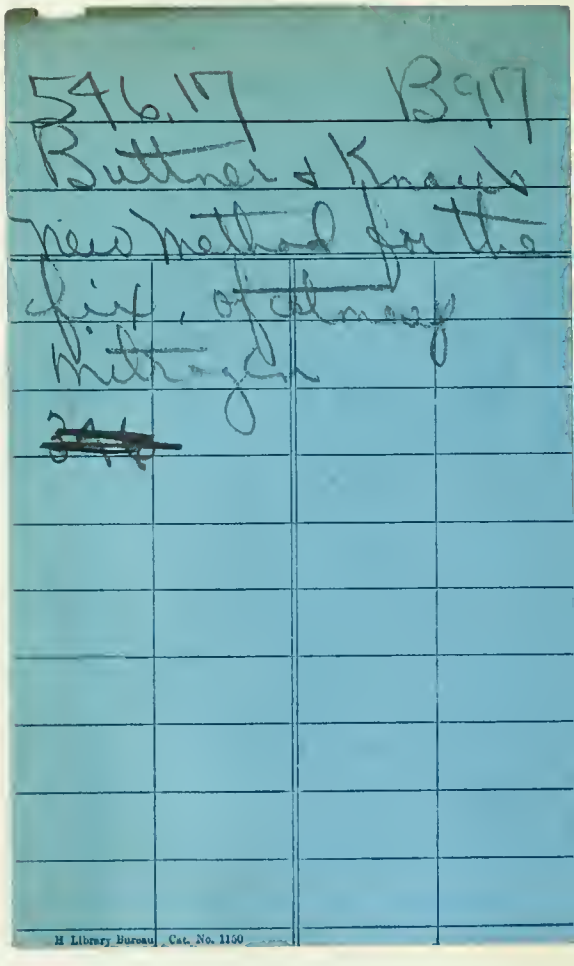
$$CaC_2 + N_2 = CaCN_2 + C$$

The reaction is exothermic and the heat given off is almost sufficient to maintain the mass at the combining temperature When the absorption is complete the can is removed and allowed to cool. The product has a blue black color with small glistening crystals of pure calcium cyanamide. The nitrogen used can be prepared either by the liquid air or the copper oxide process. The worlds production of cyanamide is estimated at 120,000 tons per annum. The basic patent protecting the process of manufacture was issued to Prof. A Frank and Dr. Nicodem Caro in 1908.

One of the true fixation processes which is rapidly coming to the front and which is now being tried on a large commercial scale, is a process first proposed by Ottokar Serpek of France. The nitrogen is fixed thru the medium of aluminium nitride. The existance of aluminum nitride had been suspected for a number of years before that substance was issolated. Aluminum nitride contains 34 percent nitrogen and it decomposes in moist air to ammonia and alumina. Serpek's first proposition was to form aluminum nitride from aluminum carbide, by passing a stream of nitrogen

over the material, heated to a red heat. He found that his yield of nitride was increased by the addition of carbon. alumina or aluminum chloride; and that the presence of HCl or SO_2 in the gas facilitated the reaction. Serpek found that a nonuniformity existed in the product formed by the reaction, and that part of the nitrogen could be driven off by contact with the air: and that a further quantity could be driven off by boiling with water, and that still more was removed by treatment with caustic alkali solution. These facts all point to the nonhomogenuity of the product, which appears to consist of several nitrides of aluminum. Serpek attempted to produce the nitride directly from aluminum and carbon mixtures. but he was not sucessful in this until he had added small amounts of copper or iron to the mixtures. The aluminum nitride was then obtained from the alloy. In his latest patents Serpek investigated the production of the nitride from Al_2O_3 and carbon mixtures. It was first supposed that the temperature at which the reaction took place would be extremely high, such as the highest temperatures of the electric furnace, but this is not true. The reaction between alumina and nitrogen can be observed at 1100° C., at 1500° C. nitrogen is absorbed rapidly and at 1800 to 1850° the reaction becomes violent. At temperatures above 2000° the reaction practically stops, as the decomposition temperature of the nitride appears to be about 2120°C. The inventor also used bauxite, which is an impure aluminum oxide. in his process and it was converted at a lower temper-

ature than the pure aluminum oxide. S. A. Tucker and H. Read in a test of the process using bauxite of 78 percent purity, found that below 1600°C the yield of combined nitrogen was trifling; but between 1600° and 2000° the maximum yield of combined nitrogen was 30.19 %. This approaches very closely to the theoretical yield, which is 34.06% . Serpek's patents in the U. S. granted June 20, 1911, contain a detailed description of the apparatus intended for the commercial manufacture of the nitride from bauxite. The plant has two superposed cylindrical kilns similar in construction to cement kilns. These are inclined in opposite directions, so that the material being preheated in the upper kiln, falls into the opening of the lower kiln for higher temperature treatment. The bauxite is placed in the upper kiln and is there calcined, and in its passage to the lower kiln is mixed with the necessary carbon and the mixture is then treated with nitrogen, at the high temperature of the lower kiln. This is provided with a detachable resistance furnace, which is intended to heat the charge to the reacting temperature. The material is charged from the end of the kiln into an air tight receiver. A large gas producer at the end of the second kiln furnishes gas of the approximate composition, one third carbon monoxide and two thirds nitrogen. This gas enters the kiln at about 400° C, passes over the descending charge and at the electrically heated zone acts on the mixture to form the nitride. The apparatus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described makes use of the CO gas of the producer and that evolved in the reaction, by burning it to heat the upper kiln. It also aims at the intimate mixture of the charge and intimate contact of the nitrogen and the charge. The process under suitable conditions of working ought to produce aluminum nitride containing 30 percent or more combined nitrogen. For the manufacture of nitrogen compounds this would give the process an advantage over calcium cyanamide, which on the average runs from 17 to 20 percent combined nitrogen. When the aluminum nitride is treated with steam ammonia is formed and pure aluminum oxide is left. This is one of the valuable products of the process.

Besides calcium and aluminum there are several other metals which will fix nitrogen. Processes have been worked out using the alkalies and the alkaline earth metals, and also such metals as titanium and silicon, but none of these seem to have any commercial significance. Most of them are in the experimental stage only. Among these is the Sinding-Larsen process. It makes use of the fact that silicon nitrogen compounds are formed, when quartz and coke are heated in an atmosphere of chlorine and nitrogen in an apparatus resembling a blast furnace.

The process on which the nitrogen fixation tests were made is a modification of another process, which is the subject of a French patent numbered 429.140, granted to M. Louis Devaucelle of France on July 7, 1911. The inventor of that process had been experimenting with the formation of cyanides, which he obtained by heating intimate mixtures of carbon and the oxide of a metal in an atmosphere of nitrogen. The cyanide was formed according to the following equation.

$$MO + 3C + N_2 = M(CN)_2 + CO$$

This product when treated with superheated steam will decompose, liberating ammonia and carbon monoxide, and will regenerate the oxide of the metal according to the equation.

$$M(CN)_2 + 3H_2O = MO + 2NH_3 + 3CO$$

This last part of the reaction is well known, for it is made use of in producing ammonia from cyanamide. The oxide of the metal can be used over several times but then has to be rejected, as the impurities introduced with the carbon accumulate and prevent the formation of the cyanide. The inventor used forms of carbon, containing a minimum of ash, because at the temperatures used in the process, fused silicates and aluminates would result. These would form protective coatings over the oxide of the metal and prevent the formation of the cyanide. The forms of carbon used were gas carbon and graphite,

and these always contained less than .05 % of ash. The heating of the mixture was done in closed retorts similar to those used in the cyanamide industry. The whole of the commercial operation was to be carried out in one piece of apparatus. In the first part of the operation the mixture was heated in the retort to a temperature a little lower than that at which the cyanide decomposes. Nitrogen gas was then passed into the retort until the formation of the cyanide was completed. Steam was then admitted and the ammonia formed was removed by absorption. When this reaction had been completed, the steam was shut off and a charge of carbon containing material was added to the oxide. This carbon could also be added to, by subliming naphthalene. and passing it in with the nitrogen gas. The advantages that this process would have over the cyanamide and Serpek processes are the low heat of formation of the product and the practically continuous operation of the process. The process tested by the authors was a modification of the one given above. We wanted to use the sulphide of a metal to form the sulphocyanide. The metal which has a great affinity for cyanogen compounds is iron. No simple cyanides of iron exist, owing to the great tendency of iron to form complex cyanides. Substances described as $Fe(CN)_2$ have always proven to be ferrocyanides of iron. However both simple and complex ferrous and ferric sulphocyanides of iron exist. It was the object of this invest-

igation to find out whether these compounds would form in sufficient quantities to make the method a commercial one and under what conditions they would form. The chemistry of the process would be as follows.

$$Fe_2O_3 + S + 2C + H_2 = Fe_x(CNS)_y + CO$$

The product would probably be of indefinite composition and this is indicated by the x and y. On treating such a product with steam an oxidation would no doubt occur, and if this was sufficiently high the product would be ammonium sulphate, the most marketable product of NH3. A very good starting material was also found for testing out this process and this material consisted of an intimate mixture of different organic substances together with iron oxide and sulphur. This substance is the spent iron oxide used in the purification of illuminating gas from sulphur compounds. It has no industrial use and it is regarded as a nuisance by the gas companies, who have to pay to have it removed. Its only use seems to be as a filling material.

Iron oxide shavings have been used for a number of years in the gas works for purifying gas, and although the method is not the most efficient one for removing sulphur compounds, still it is the least objectionable of the many that have been tried. The chemistry upon which the removal of sulphur compounds in illuminating gas depends is as follows. When hydrogen sulphide or

carbon disulphide, these being the two prevalent sulphur compounds in illuminating gas, is passed over hydrated iron oxide in the presence of traces of ammonia, iron sesquisulphide is formed. Coal gas always contains ammonia to a small extent. In order to insure sufficient porosity and sufficient surface for reaction, the iron oxide is suspended on wood shavings. These also serve the purpose of being the catchers of the final traces of tar in the gas. The oxide is placed in layers several feet thick in the purifying boxes, and thru it the gases must pass. After passing thru several of these boxes in series the sulphur compounds will have been removed fairly well. After the oxide has been used in the purifying boxes for some time, it becomes foul and ceases to act as a sulphide remover. It is then taken out, spread on the ground and aired for several days. It then can be used in the purifying boxes again. This airing is repeated several times, until the sulphur content becomes so high that it cannot be used any more and it is then discarded. The airing process is a straight oxidation, for it decomposes the Fe_2S_3, giving free sulphur and Fe_2O_3; and this Fe_2O_3 is again active in removing sulphur compounds. The equations for the decomposition and formation of the sesquisulphide of iron are as follows.

$$Fe_2O_3 + 3H_2S = Fe_2S_3 + 3H_2O$$

$$Fe_2S_3 + 3\,O = Fe_2O_3 + 3S$$

The spent iron oxide and original oxide used in the tests was obtained from the 31 st. St. plant of the Peoples Gas Light and Coke Co. The spent oxide was obtained from different parts of a large pile of that material in the yards of the gas plant. The material had been lying there for several months and it was quite wet. It had been exposed to the weather and the surface of the heap was brown in color, due to the oxidation of the iron, but the interior was black in color and showed small glistening plates of naphthalene. The heap of material was sampled in different parts in order to get a uniform sample for analysis. This material was taken to the laboratory and quartered and an analysis was made for moisture and iron as soon as possible. The spent oxide shavings had the strong odor of naphthalene and tar. Moisture determinations were made by placing weighed samples of the material in aluminum dishes and heating them in a drying oven for three hours at 102° C. The difference in weight of sample can not properly be designated as moisture alone, as some of the other organic material is volatile at that temperature and was undoubtedly driven off. As this temperature is above the melting point of naphthalene, that constituent melted and a small portion of it no doubt sublimed. The material was analysed for iron by slowly igniting a weighed sample of it over a blast lamp, until all of the organic material

and free sulphur had been driven off, and then dissolving the residue in acid and determining the iron content by titration with $KMnO_4$ solution.

Moisture and volatile matter at 102°C - 24.5 %

Iron . . . . . - 11.7 %

The original iron oxide shavings as bought by the gas works was analysed with the following results.

Moisture . . . . - 1.6 %

Ferric oxide . . .. - 72.2 %

Wood (by difference) . - 26.2 %

The spent iron oxide as obtained from the gas works was too wet to be used in any tests, so it was first dried for three hours at a temperature of 50°C. This was done in shallow pans in a steam drier. During the drying operation the material was stirred from time to time. On conclusion of the drying the material was placed in bottles and a uniform sample was taken for analysis. Analyses were made for moisture and volatile matter, iron, total sulphur, free sulphur, nitrogenous matter, other organic material and wood. The organic material present was further investigated by extractions to determine its constituents. The iron, moisture and volatile were determined exactly as in the wet oxide. Total sulphur was determined by decomposition and oxidation of the material with fuming nitric acid, and then determining the sulphur gravimetrically as barium sulphate.

Nitrogenous matter was determined by decomposing the material with sulphuric acid, potassium sulphate and mercuric oxide in a Kjeldahl flask. The nitrogen was then converted to NH_3 and determined by distilling into a standard acid solution. Free sulphur and organic material were determined by extraction with different solvents. The sulphur was then determined gravimetrically in the extracts. The residue was then analysed for the combined sulphur. Another sample of the residue was slowly ignited and its loss in weight was recorded. This corresponds very closely with the percent of wood present.

Moisture and volatile	- 7.17 %
Total iron	- 17.70 %
Total sulphur	- 31.70 %
Extracted organic matter and free sulphur. . . .	- 43.84%
Sulphur in residue	- 1.34 %

After the moisture and volatile had been determined, the samples were placed in extraction thimbles and extracted with different solvents. The apparatus used consisted of small extraction flasks, Soxhlet tubes and reflux condensers. The apparatus when set up appeared as in figure 1. For light solvent extractions the heat was furnished by incandescent lamps, while heavy solvents were heated directly by a Bunsen flame. The solvents used were ether, alcohol. acetone, carbon tetrachloride and carbon disulphide.

These were used one after another in the order named, and were effective in removing the following things.

Ether- removed all of the naphthalene and light oils and some of the heavy oils and tar.

Alcohol- removed oils and tar.

Acetone- removed free sulphur and tar.

Carbon tetrachloride- removed free sulphur and other organic matter.

Carbon disulphide- removed free sulphur and organic sulphur compounds.

When ether was used in the cold, it would remove only naphthalene and a little oil and the extract after the ether was evaporated was a light grey solid. When the extractions were made hot, practically all of the oils were removed and the naphthalene crystallized out of the oils. The crystals were dried on filter paper and weighed and thus the approximate percent of naphthalene was determined. The sample used at the beginning of these extractions was always ten grams. The results obtained from one of these extractions when ether, acetone and carbon disulphide were used as solvents is as follows.

Moisture and volatile	- 7.17 %
Ether extraction.	- 12.36 %
Acetone extraction	- 5.92 %
Carbon disulphide extraction . .	- 25.56 %
Residue	- 48.99 %
	100.00 %

The residue was analysed for iron and sulphur. The sulphur present was calculated to Fe_2S_3 and the remaining iron was calculated to Fe_2O_3.

Fe_2S_3	- 2.90 %
Fe_2O_3	- 23.10 %
Wood shavings	- 22.99 %
	48.99 %

The following would be a complete analysis of the spent iron oxide.

Moisture and volatile . .	- 7.17 %
Naphthalene	- 7.60 %
Oils	- 4.76 %
Tar and other organic comp.	- 1.12 %
Free sulphur	- 30.36 %
Fe_2S_3	- 2.90 %
Fe_2O_3	- 23.10 %
Wood shavings - . . .	- 22.99 %
	100.00 %

It can be seen from the analysis of this iron oxide, that it would do very well as the material for carrying out our process of nitrogen fixation, if it were not for the high sulphur content. We did not expect the material to carry as high a percentage of sulphur as it did. We also expected more of the sulphur to be combined with the iron and very little of it to be there as free sulphur. However we took the material as it was and went on with our tests of nitrogen fixation.

Preliminary tests.

In order to determine at what temperatures and under what conditions the reaction for the fixation of nitrogen would take place, if it would take place at all. we deemed it advisable to make preliminary tests using small samples of oxide. These tests were made in an ordinary gas heated combustion train and a hard glass tube. In this apparatus temperatures up to 600°C were obtained. Gram samples of material in shallow alundum boats were placed in the tube. This was connected to a nitrogen tank thru a pressure regulator and a continuous stream of nitrogen was passed over the hot oxide. The nitrogen used was obtained from the Linde Air Products Co., who manufacture it by the fractional distillation of liquid air. The gas on analysis showed that it was over 99 % pure. A series of boats with samples were placed in the tube and removed one by one as the temperature rose. Those subjected to the highest temperature however were left to cool slowly in a stream of nitrogen. Temperature measurements were taken with a direct reading pyrometer. In the first series of tests we used a mixture spent oxide, fresh oxide and carbon. This was done to increase the iron content and to lower the sulphur content. The following mixture was used.

10 grams of spent oxide.

90 " " fresh " .

10 " " wood charcoal.

After the oxide had been heated in an atmosphere of nitrogen for some time it was cooled , placed in a Kjeldahl flask and decomposed to determine the combined nitrogen.

Table shows results of the first preliminary test.

SAMPLE.	MAXIMUM TEMPERATURE.	MINUTES HEATED.	PERCENT NITROGEN
1	500° C.	32	0.29 %
2	550	45	0.21 %
3	600	68	0.18 %
4	650	68	0.19 %

These results show that no nitrogen was being absorbed. The spent oxide alone contains combined nitrogen to the extent of 0.30 %, but as the spent oxide in this mixture would only furnish 0.03 % nitrogen, the remaining 0.16 to 0.26 % of fixed. This amount is too small however to be considered. Our next tests consisted of using spent oxide alone and heating it to a higher temperature than we could attain in the combustion train. We also found that as the material became red hot the excess sulphur and organic matter distilled off. In order to obtain the higher temperature an electric resistance furnace and fused silica tube were used. In each of the runs made the sample was heated up to the proper temperature and was then allowed to slowly cool in a stream of nitrogen. Thus if there had been a nitrogen compound formed and the temperature had risen above the decomposition temperature of that compound, the compound would

be reformed, as the material slowly cooled in the stream of nitrogen. Five runs were made, the results of which are shown below.

SAMPLE	MAXIMUM TEMPERATURE.	MINUTES HEATED.	PERCENT NITROGEN.
1	720° C.	90	0.21 %
2	820	90	0.20 %
3	850	110	0.20 %
4	900	110	0.19 %
5	950	90	0.17 %

The arrangement of the apparatus for this test can be seen in figure 2. The outgoing gas was placed in a holder during a run, and an analysis was made of it with the following results.

Carbon dioxide - 10.0 %
Oxygen . . . - 0.8 %
Carbon monoxide - 0.2 %
Nitrogen . . - 89.0 %

From the results given above it can be seen that no nitrogen at all was absorbed at the higher temperatures. Our next tests were made on mixtures of the spent oxide and KOH, Na_2CO_3 and CaO. The intention this time was to see if complex salts of these metals and iron would not fix nitrogen. These mixtures were made and used as follows.

Mixtures :-

1. ---- 1 g. Spent oxide, -- 0.5 g. KOH,-- 0.1 g. carbon.
2. ---- " " " -- 0.5 g. " -- " " .
3. ---- " " " -- 0.5 g. Na_2CO_3- " " .
4. ---- " " " -- 0.5 g CaO -- " " .

These mixtures were to different temperatures in the combustion train and the electric furnace in atmospheres of nitrogen. The nitrogen determinations made on the above were made on the basis of one gram of spent oxide and all percentages are so calculated. This was done in order that all results would be on the same basis and that comparisons could be made. The results of the test with mixtures is given below.

MIXTURE	MAXIMUM TEMPERATURE.	PERCENT NITROGEN.
1	400° C.	0.21 %
2	800	0.18 %
3	400	0.17 %
4	400	0.19 %

These tests satisfied us that the desired reaction would not take place under the temperatures and conditions used. Our next tests were made with the application of temperature and pressure.

Tests using high temperature and pressure.

The retort used to make these tests in was especially designed for the purpose. It was rectangular in shape, and just the proper size to fit into the large gas fired roasting furnace that we were going to use. The retort was made of lap welded wrought iron with a front cover plate held on by stud bolts. The retort and piping layout can be seen in fig. 4 and also in the photographs. In order to get good pressure regulation, two valves were used in the pipe between the nitrogen tank and the retort, and only one valve was used in the exit pipe. A pressure gauge was placed in the exit tube and this would show the pressures in the retort. This gauge was calibrated just before the test was made and the calibration curve, plate III, shows it to be fairly accurate. In these pressure tests we used four different mixtures.

1. --- 100 g. spent oxide, -- 68 g. KOH, --- 5 g. carbon.
2. --- " " " -- 75 g. K_2CO_3 -- " " .
3. --- " " " -- 35 g. CaO ---- " " .
4. --- " " " -- 70 g. $CaCO_3$ -- " " .

The mixture was placed in the retort in a clay dish, the cover was then carefully bolted on over the asbestos gasket and the pipe connections with the nitrogen tank were made. When everything was ready the gas burner was started and the temperature was brought up slowly, as the temperature curve shows. A continuous stream of nitrogen was allowed to pass thru the apparatus, in order to drive out the sulphur

fumes that were liberated as the temperature rose. The temperature of the retort was determined by a thermocouple. When the temperature reached 700° C., the exit valve was closed and a pressure of 20 pounds was allowed to remain on the retort. By this time alloff the sulphur fumes had been driven off and after the 20 pound charge had been discharged a fresh charge of 120 pounds was put on and held there for one half hour. The temperature of the retort was then 700°C. The gas was then turned o f and the retort was allowed to come back to room temperature with the nitrogen pressure still on.

The resulting weights of the four samples were as follows:

SAMPLE	ORIGINAL WT.	FINAL WT.	LOSS IN WT.
1	173 grams.	98.3 grams	74.7 grams.
2	180 "	105.3 "	74.7 "
3	140 "	81.7 "	58.3 "
4	175 "	113.8 "	61.2 "

Gram samples of the final product were used for nitrogen determinations, the results of which are given below.

SAMPLE	PERCENT OF NITROGEN.
1	0.292 %
2	0.271 %
3	0.262 %
4	0.193 %

The last results obtained show that only very little if any nitrogen was fixed. It is evident that pressure will not help the fixation if the proper temperature has not been reached in the first place. No tests at higher temperatures than 1000° C. were made on the material, because the reaction was intended as a low temperature one, and secondly because we did not have the apparatus necessary to produce a higher temperature.

After the preliminary and pressure tests had been completed, a carefull inspection of the data showed that the amount of nitrogen fixed was practically negligible. The process evidently does not work under the conditions MAINTAINED DURING THE TEST. As the original idea was to use comparatively low temperatures, that is under 1000° C., no tests were made at temperatures above this point. Also no other materials were used other than spent oxide, the idea being to use for the process a material which could be obtained very cheaply. In view of these facts, the authors have come to the conclusion, that the utilization of spent oxide as a basis for the fixation of nitrogen is impossible.

We desire to acknowledge our indebtedness to Professor H. McCormack for his valuable suggestions offered during the work.

We are further indebted to Mr. Hallam C. Smith of the Peoples Gas Light and Coke Co. for his assistance in obtaining supplies of iron oxide shavings: and to Mr. E. W. Mc Mullen for the many valuable suggestions offered.

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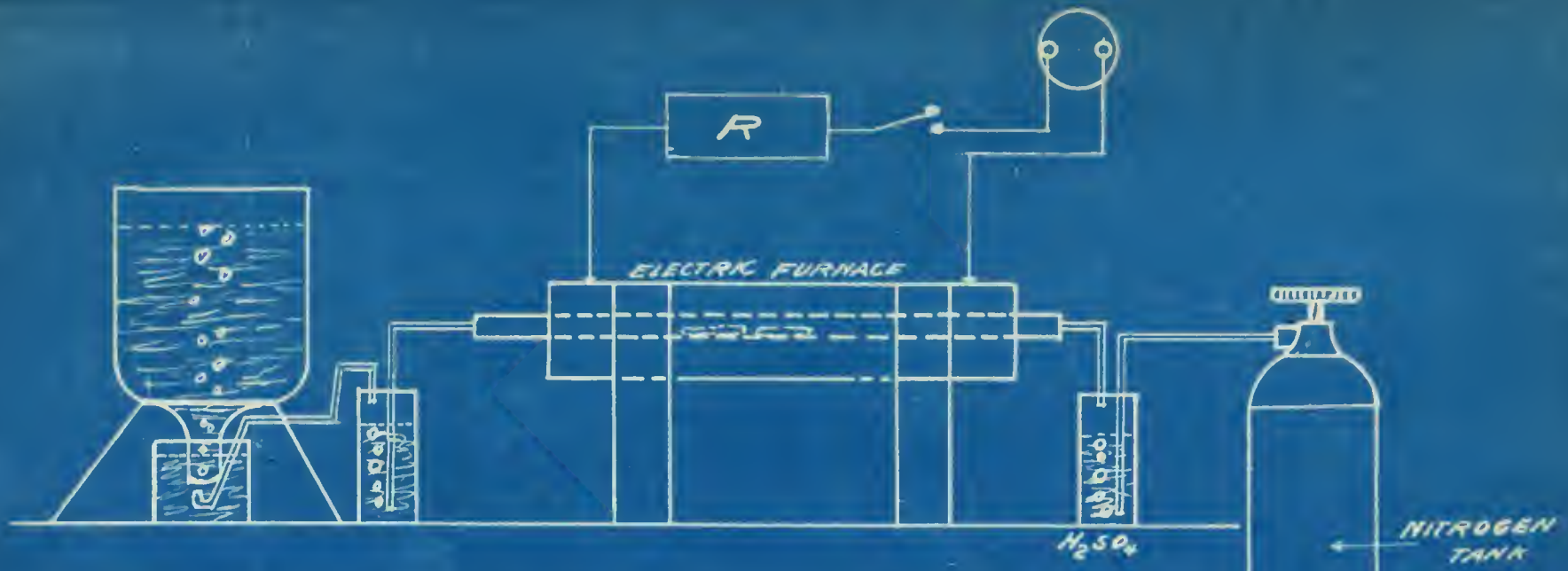


Layout Of Apparatus Used In Preliminary Tests.

Plate I.

PLATE II

TEMPERATURE CURVE OF RETORT DURING RUN.

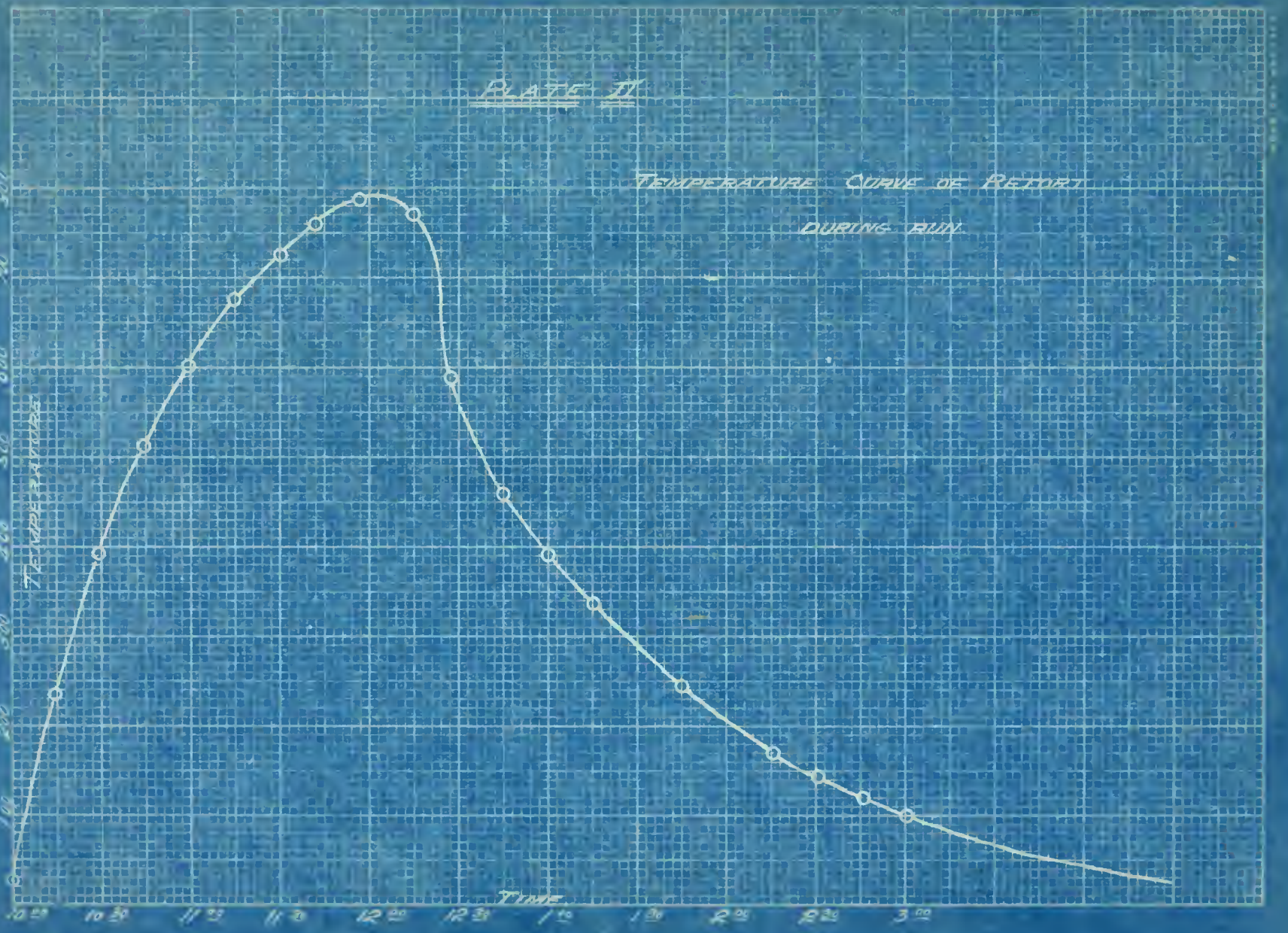
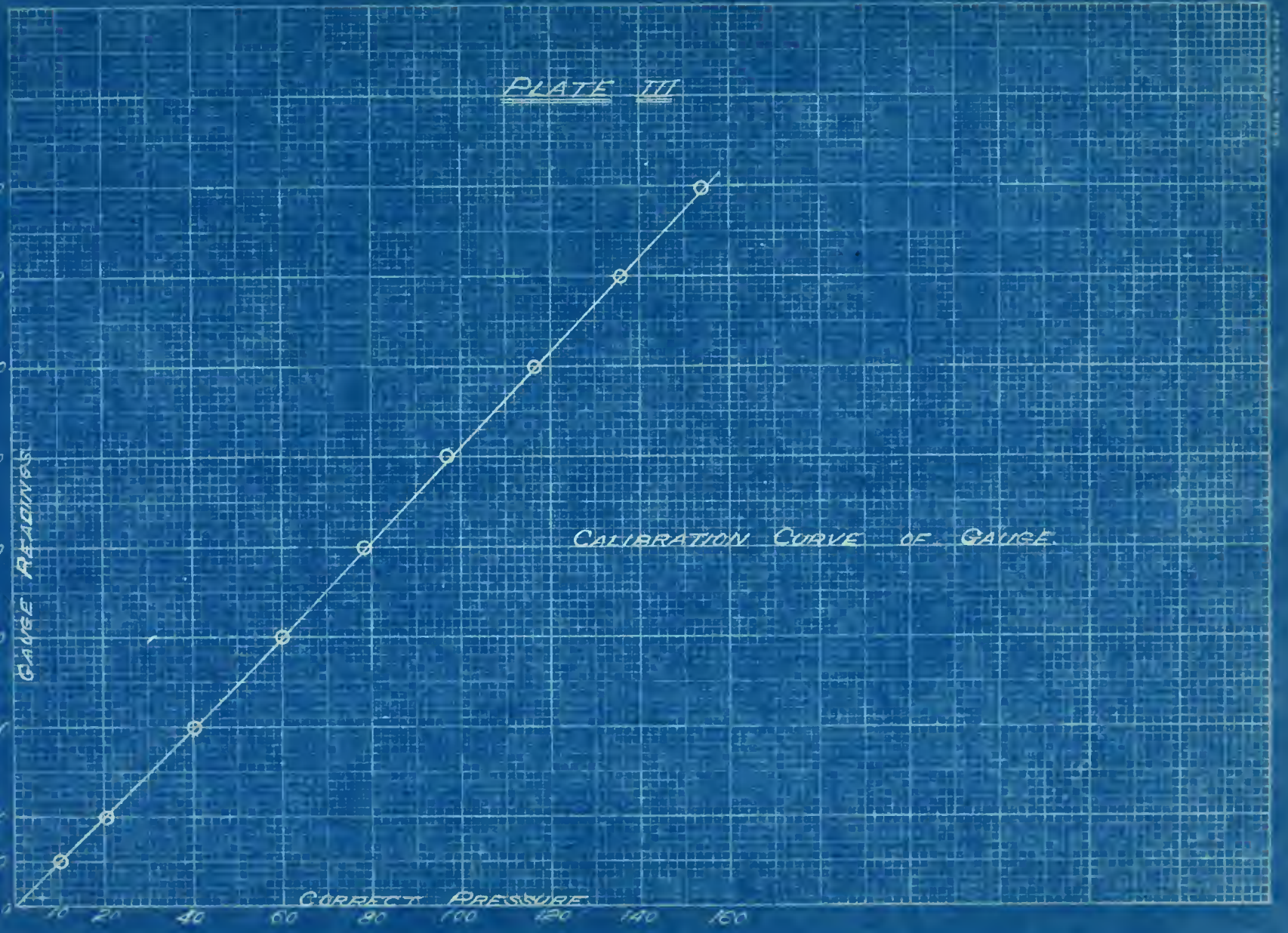
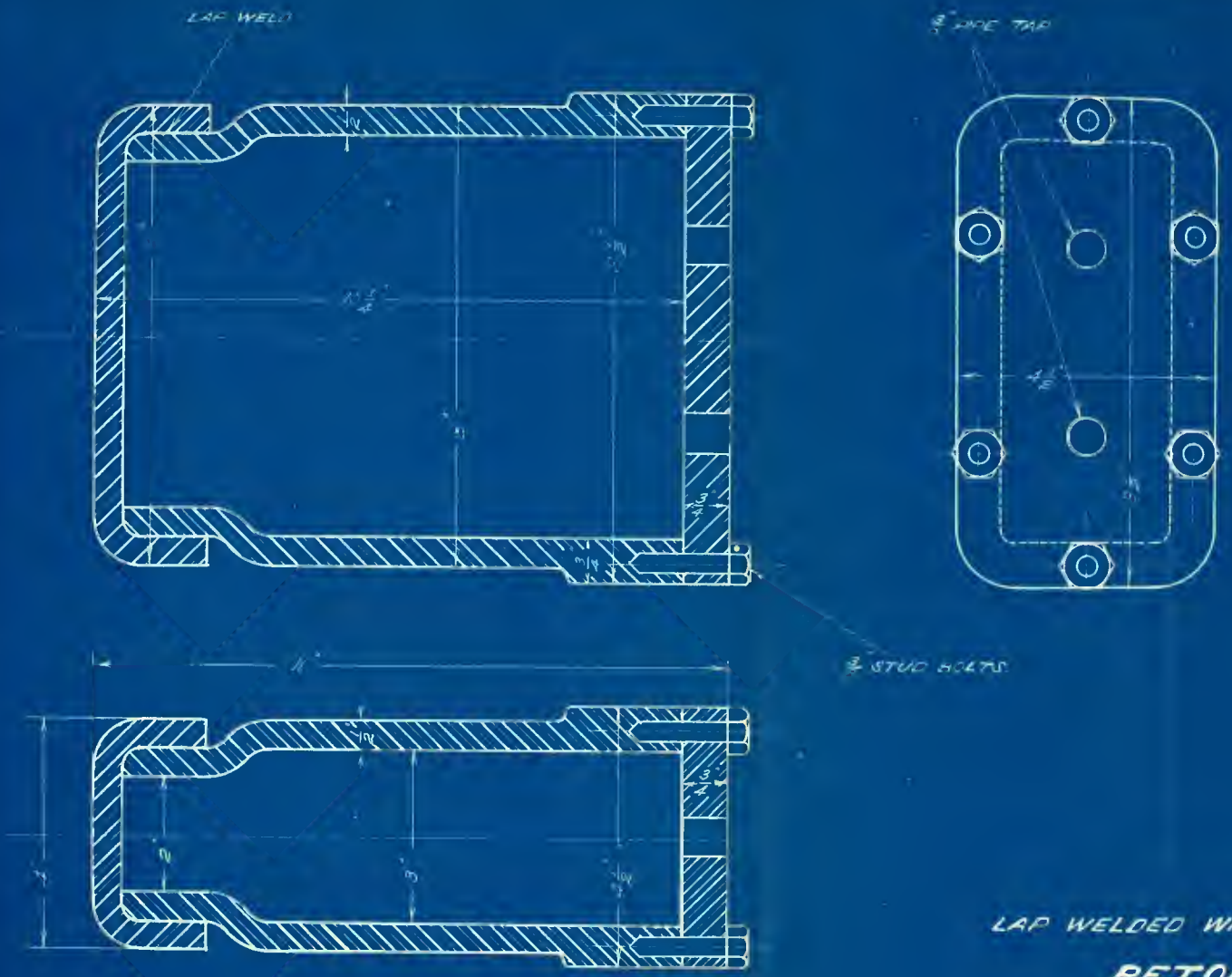


Plate III


Gauge Readings
0
10
20
40
60
80
100
120
140
160
Correct Pressure
Calibration Curve of Gauge.



LAP WELDED WROUGHT IRON

RETORT

ARMOUR INSTITUTE OF TECHNOLOGY.

CHEMICAL ENGINEERING DEPT.

FEB. 21, 1913.

FIGURE I

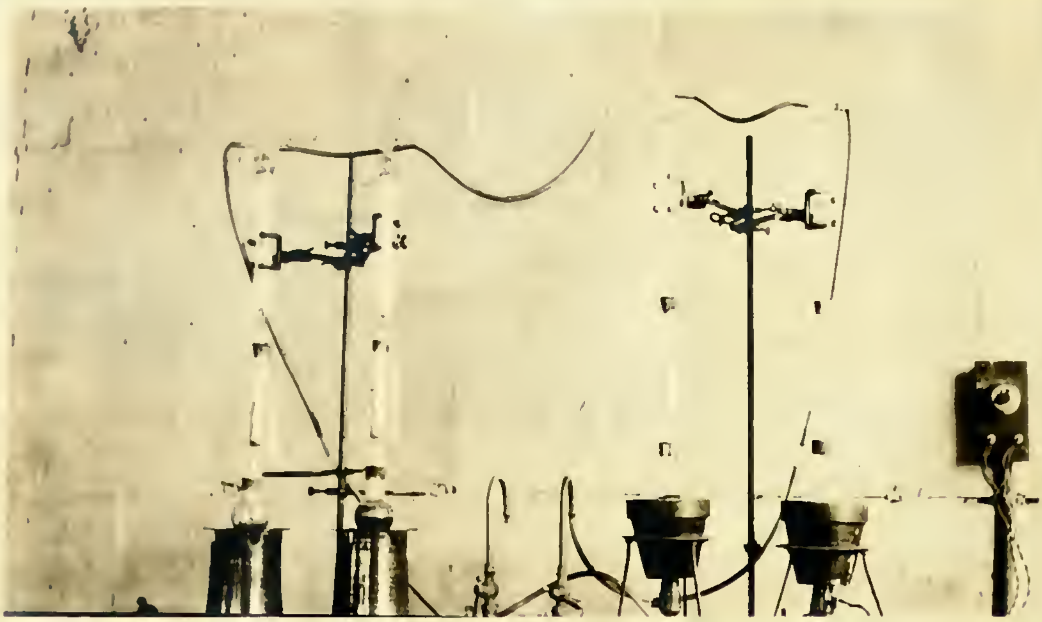


FIGURE II

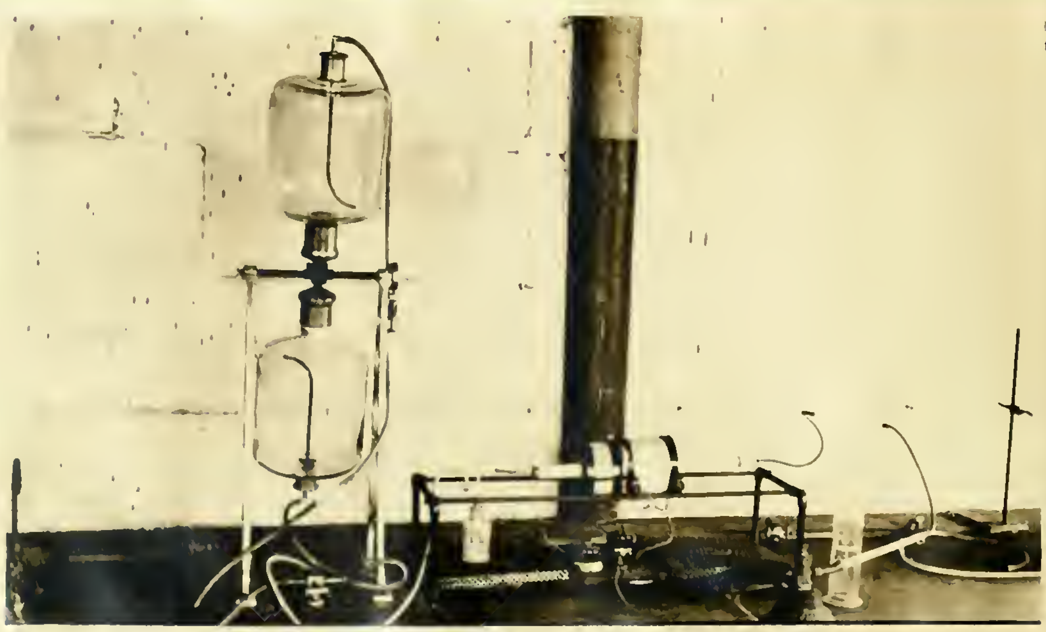


FIGURE III

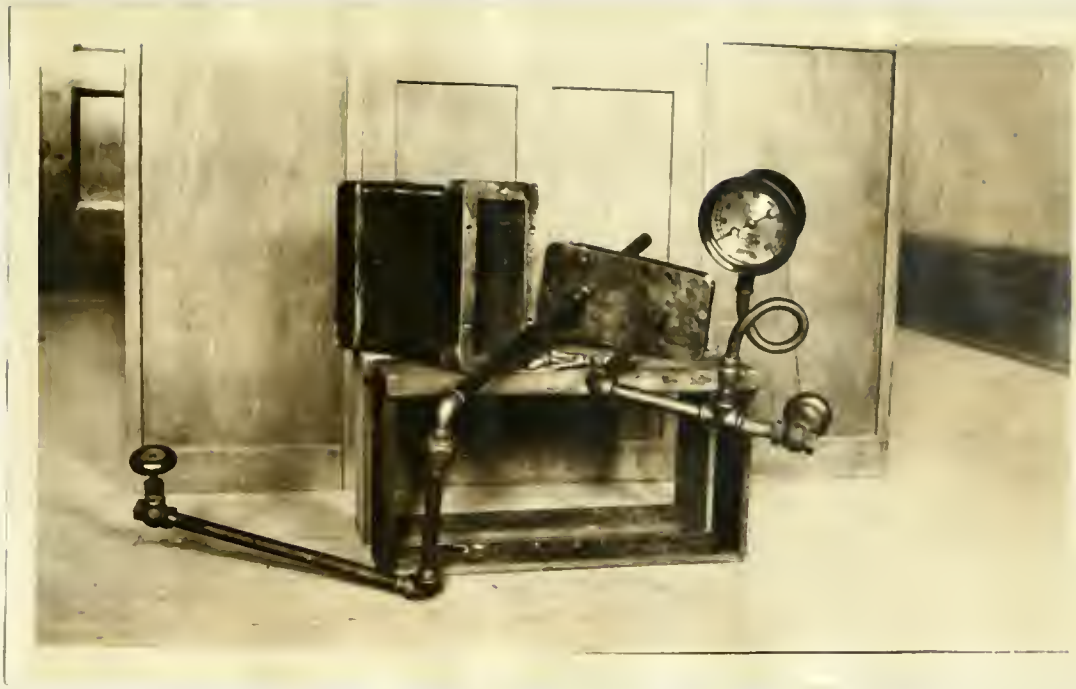


FIGURE IV.